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Cyclopentadienyl C–H Activation in Zirconocene Phosphide Complexes

Jianwei Ho and Douglas W. Stephan*

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

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Summary: Generation of "Cp_2Zr" in the presence of $PhPH_2$ results in P–H activation, affording the intermediate $Cp_2Zr(PPhH)H$. C–H activation and subsequent C–C bond formation yield the Zr(III) diphosphide- and fulvalenide-bridged complex $[(\eta^5\text{-}Cp)Zr(\mu^2\text{-}PPhH)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4C_5H_4)]_2$ (**1**). In the analogous reaction employing $(2,4,6\text{-}t\text{-}Bu_3C_6H_2)PH_2$, the isolated product is the trimeric, phosphide-capped Zr(IV) species $((\eta^5\text{-}Cp)(\mu\text{-}\eta^1{:}\eta^5\text{-}Cp)Zr)_3(\mu^3\text{-}P)$ (**2**). C–H activation is evident as metalated Cp rings bridge adjacent Zr atoms in a $\eta^1{:}\eta^5$-fashion. This compound **2** also represents a rare example of a trinuclear organometallic species containing a capping phosphorus atom. Further, the structure of **2** implies a mechanism for the formation of **1** involving the initial formation of a dimer in which the Zr centers are linked by $\eta^1{:}\eta^5$-Cp moieties.

Despite the fact that the first metallocene Zr(IV) (i.e. $Cp_2Zr(PR_2)_2$) and M(III) ($[Cp_2M(PR_2)]_2$, M = Ti, Zr) phosphide complexes were formulated in the middle 1960s,[1] group 4 phosphides have drawn little attention in comparison to the analogous metal amide systems.[2] It was not until 1983 that Baker et al. published the first definitive spectroscopic and structural characterization of group 4 phosphide complexes of the form $Cp_2M(PR_2)_2$.[3] Since then, other workers have reported similar compounds,[4–6] while Baker et al. have also reported the homoleptic early-metal phosphide complexes $Li[M(PCy_2)_5]$ (M = Zr, Hf) and $Li[M(PCy_2)_4]$ (M = Ti, V).[7] Subsequent studies by the research groups of Bercaw,[8] Gambarotta,[9] Hey,[10] and Hillhouse[11] have described related species of the form $Cp^*Hf(PR_2)X_2$ (X = Cl, R, H), $[Cp_2M(\mu\text{-}PR_2)]_2$, $Cp_2M(PR)_3$, and $Cp_2M(PRH)X$ (M = Zr, X = Cl; M = Hf, X = Cl, H), respectively. Most recently we[12,13] and others[14] have investigated the di- and mononuclear titanocene phosphide systems $[Cp_2Ti(\mu\text{-}PR_2)]_2$, $Li[Cp_2Ti(PR_2)_2]$, $Cp_2Ti(PR_2)(PMe_3)$, and $Cp_2Ti(PR_2)$.

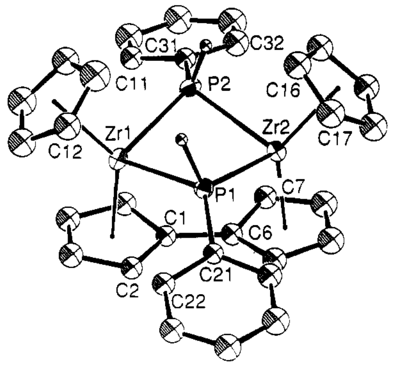

Figure 1. ORTEP drawing of 1 in the asymmetric unit. Thermal ellipsoids at the 30% level are shown. All hydrogen atoms except those on phosphorus are omitted for clarity. Zr1–P1 = 2.627 (4) Å, Zr1–P2 = 2.610 (4) Å, Zr2–P1 = 2.609 (4) Å, Zr2–P2 = 2.620 (4) Å, P1–C21 = 1.83 (1) Å, P2–C31 = 1.84 (1) Å; P1–Zr1–P2 = 90.5 (1)°, P1–Zr2–P2 = 90.7 (1)°, Zr1–P1–Zr2 = 85.4 (1)°, Zr1–P2–Zr2 = 85.5 (1)°, Zr1–P1–C21 = 127.7 (5)°, Zr2–P2–C31 = 128.1 (5)°.

Much of the known chemistry of early-metal phosphides centers on the use of such species as synthetic precursors to early–late heterobimetallics.[15] As part of our efforts to more fully examine the chemistry of early-metal phosphides, we have recently employed complexes of the form $Cp_2Zr(PRH)H$ as precursors to phosphido- and phosphinidene-bridged dimers.[16] We now wish to report results which demonstrate that, in some instances, the Lewis acidity of complexes of the form $Cp_2Zr(PHR)H$ may invoke activation of C–H bonds in the ancillary cyclopentadienyl rings and in some cases result in subsequent C–C bond formation.

The reaction of Cp_2ZrCl_2 with 2 equiv of *n*-BuLi in THF at –78 °C with subsequent warming to 25 °C has been used as a means of generating zirconocene in situ.[17] Reaction of "Cp_2Zr" with $PhPH_2$ results in a darkly colored solution which upon workup affords black crystals of 1 in a isolated yield of 25%. The ^1H NMR spectrum of 1 shows resonances at 7.1, 5.49, 4.76, and 3.97 ppm attributable to phenyl, cyclopentadienyl, and fulvalenide moieties.[18] No

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[17] (a) Swanson, D. R.; Negishi, E. *Organometallics* **1991**, *10*, 825. (b) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. The species Cp_2ZrH is proposed as an intermediate in the Mg reduction of Cp_2ZrCl_2 arising from cyclopentadienyl C–H activation by "Cp_2Zr". (Samuel, E. *Inorg. Chem.* **1983**, *22*, 2967.) While the role of this species in the formation of 1 and 2 cannot be eliminated, it is noted that the formation of Cp_2ZrH requires 48 h, whereas evidence of P–H activation by "Cp_2Zr" is observed upon addition of phosphine.

[18] Spectral data for 1: ^1H NMR (C_6D_6, 25 °C) δ 7.1 (br m, Ph), 5.49 (s, Cp), 4.76 (pseudotriplet, $C_{10}H_8$), 3.97 (pseudotriplet, $C_{10}H_8$), $|J_{H-H}|$ = 3.6 Hz; $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C) δ 137.77, 136.74, 129.07, 125.42 (Ph), 95.36 (Cp), 113.97, 93.71, 87.60 ($C_{10}H_8$). Anal. Calcd: C, 58.33; H, 4.59. Found: C, 58.10; H, 4.30. Spectral data for 2: ^{31}P NMR (THF, 25 °C) δ 782.6 ppm (relative to 85% H_3PO_4); ^1H NMR (C_6D_6, 25 °C) δ 6.21 (s, Cp), 5.65 (m, 2 H), 5.20 (m, 2 H). Anal. Calcd: C, 52.06; H, 3.93. Found: C, 51.90; H, 3.80.

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^{31}P resonance was observable at 25 °C. A crystallographic study of 1 showed it to be the species $(CpZr(\mu\text{-}PHPh))_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)$.[19] An ORTEP drawing is shown in Figure 1. This dimeric Zr(III) species contains CpZr moieties which are bridged by two phenylphosphido groups as well as a fulvalenide moiety. The fulvalene ligand is slightly bent with a 7.9° angle between the planes of the rings which are linked at C1–C6 (1.47 (2) Å). A small twist between the adjacent rings is evidenced by the dihedral angles C2–C1–C6–C10 = -5 (2)° and C5–C1–C6–C7 = 4 (2)°. This twist is more significant than that seen in $(CpZr(\mu\text{-}Cl))_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)$[20] and is attributed to the steric demands of the bridging phosphido groups. The Zr–P bond lengths were found to average 2.616 (6) Å, which is slightly shorter than the 2.672 (5) Å found in the Zr(III) dimer $[Cp_2Zr(\mu\text{-}PMe_2)]_2$.[9] This may be attributed in part to the presence of the fulvalene ligand in 1, although the basicity and the orientation of the phenyl substituents on the P atoms toward the fulvalenide rings also accomodate stronger Zr–P bonding. The P–Zr–P angles are found to be 90.5 (1) and 90.7 (1)°, while the Zr–P–Zr angles are 85.4 (1) and 85.5 (1)°. These features are similar to those found in the related Zr(III) dimer $[Cp_2Zr(\mu\text{-}PHCy)]_2$;[16] however, the Zr_2P_2 core of 1, unlike that of $[Cp_2Zr(\mu\text{-}PHCy)]_2$, is not planar; rather, the angle between the ZrP_2 planes is 30.60°. The observed diamagnetism of 1 is consistent with antiferromagnetic coupling of the Zr(III) centers, which are 3.549 (2) Å apart. Previous studies of phosphido-bridged Zr(III) dimers suggested a through-ligand mechanism[12] for such coupling, although a through-space or "super-long" bond rationale has also been proposed.[21] In the present compound 1, a ^{31}P resonance and ^1H resonances attributable to the P–H hydrogen atoms were not observed. These observations as well as the location of the P–H hydrogen atoms in the crystallographic study confirm the formation of 1 as a Zr(III) dimer and suggest a through-ligand mechanism of antiferromagnetic exchange may be operative.

In a related reaction, Mg was employed to reduce Cp_2ZrCl_2 in the presence of 1 equiv of $(2,4,6\text{-}t\text{-}Bu_3C_6H_2)PH_2$ in THF at 25 °C. The solution became dark brown, and the solvent was removed and replaced with benzene. Upon the slow diffusion of hexane into the solution brown crystals of 2 were deposited in approximately 10% yield. The $^{31}P\{^1H\}$ NMR spectrum shows a single resonance at 782.6 ppm. Moreover, the ^{31}P spectrum shows no evidence of P–H coupling, suggesting the loss of both hydrogen atoms from the phosphorus atom. The ^1H NMR spectrum shows only resonances attributable to cyclopentadienyl protons; however, it also shows that both η^5 and $\eta^1{:}\eta^5$ cyclopentadienyl rings are present. These data together with those from combustion analyses suggested the empirical formulation of $(Cp_2Zr)_3P$.[18] An X-ray structural study[19] was essential in the determination of the precise molecular architecture of 2. The results of the crystallographic study are depicted in Figure 2. The compound 2 crystallizes in the space group $R\bar{3}$ with two independent molecules in the unit cell. Thus, each of the molecules sits on a crystallographically imposed 3-fold axis. Each Zr center is π-bonded to two cyclopentadienyl rings. In addition, one of the rings is σ-bonded to the adjacent Zr atom. Thus, by virtue of the 3-fold symmetry, three σ–π cyclopentadienyl rings bridge the three Zr atoms. Completing the coordination sphere of the three Zr atoms is a single capping phosphorus atom.

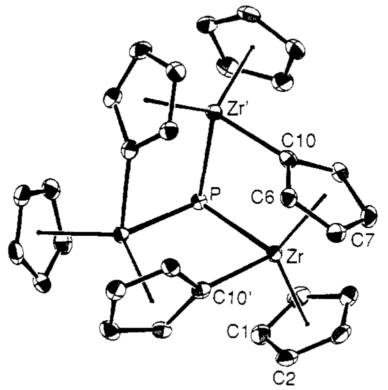
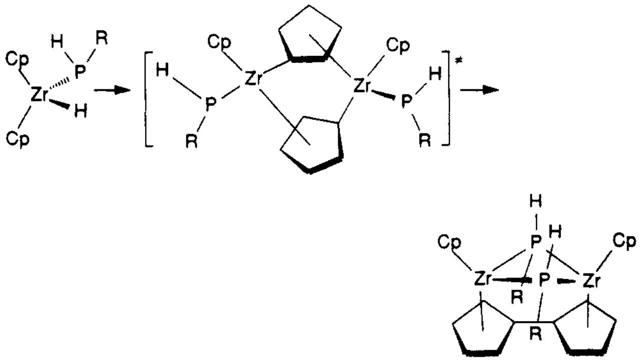


Figure 2. ORTEP drawing of molecule 2. Thermal ellipsoids at the 30% level are shown. Hydrogen atoms are omitted for clarity. Zr1–P1 = 2.575 (1) Å, Zr1–C10 = 2.288 (4) Å; Zr1–P–Zr1′ = 90.14 (5)°, P–Zr1–C10 = 87.1 (1)°.

Scheme I



The Zr–C distances to the π-cyclopentadienyl ring are typical, averaging 2.531 (6) Å, while the Zr–C σ-bond is 2.288 (4) Å. The Zr–P distance is 2.575 (1) Å, which is shorter than the Zr–P distances in either $Cp_2ZrCl(\mu\text{-}P\text{-}(2,4,6\text{-}Me_3C_6H_2))ZrClCp_2$ (2.617 (6) Å) or $[Cp_2Zr(PCyH)]_2$ (2.646 (4) Å).[16] The Zr⋯Zr separation is 3.6463 (8) Å, which is much longer than the W–W distances seen in the P-capped tungsten trimer $W_3(\mu_3\text{-}P)(\mu\text{-}OCH_2\text{-}t\text{-}Bu)_3(OCH_2\text{-}t\text{-}Bu)_6$ (W–W bonds: 2.757 (1) Å).[22] The Zr–P–Zr′ angle is 90.14 (5)°. This is much smaller than the angles of 108.6 (7)° seen in $[CpCo(\mu\text{-}P)]_4$, where the P atoms also cap three metal centers.[23] Conversely, the Zr–P–Zr′ angle in 2 is significantly smaller than the W–P–W′ angles seen in $W_3(\mu_3\text{-}P)(\mu\text{-}OCH_2\text{-}t\text{-}Bu)_3(OCH_2\text{-}t\text{-}Bu)_6$ (71.3 (1)°).[22] These

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(19) Crystal data: 1, $C_{32}H_{30}P_2Zr_2$, black blocks, triclinic, space group $P2_1/n$, $a = 9.998$ (3) Å, $b = 16.560$ (10) Å, $c = 16.794$ (5) Å, $\beta = 95.69$ (3)°, $V = 2766$ (4) Å^3, $D_c = 1.58$ g cm^{-3}, $Z = 4$, $\mu = 8.744$ cm^{-1}; 2, $C_{30}H_{27}PZr_3{\cdot}C_6H_6$, brown blocks, tetragonal, space group $R\bar{3}$, $a = 14.681$ (2) Å, $c = 23.928$ (3) Å, $V = 4466$ (1) Å^3, $D_c = 1.717$ g cm^{-3}, $Z - 6$, $\mu = 10.909$ cm^{-1}. Mo Kα radiation (λ = 0.710 69 Å) was used. Crystals were sealed in 0.5-mm capillaries under N_2 for crystallographic study. A Rigaku AFC6-S four-circle diffractometer was employed to collect the data (2θ range 4.5–50°) in each case. Three standards were collected every 150 reflections and in each case showed no evidence of crystal decay. The initial solutions for both structures were obtained from the automated Patterson solution portion of SHELXS-86 and remaining atoms found and refined by employing the TEXSAN software package from MSC running on a VAX 3520 workstation. The positions of the hydrogen atoms in the cyclopentadienyl and phenyl groups in 1 and 2 were calculated and their contributions included but not refined. In the case of 1, the hydrogen atoms on phosphorus were located in a difference map at 1.40 Å from P. Refinement: 1, 1885 data with $I > 3\sigma(I)$, 225 variables, $R = 0.0567$, $R_w = 0.0570$, GOF = 1.494; 2, 1295 data with $I > 3\sigma(I)$, 124 variables, $R = 0.0291$, $R_w = 0.0341$, GOF = 1.122. In each case a final difference map showed residual electron density of no chemical significance.

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structural features of **2** result in a canted orientation of the Cp_2Zr units about the P atom. This precludes π-interaction between the acceptor $1a_1$ orbital on the Cp_2Zr fragments with the lone pair of electrons on P and thus suggests that the capping P atom should be an effective Lewis base. Reactivity studies addressing this issue are in progress.

The mechanisms of the formation of **1** and **2** are the subject of interest. It is clear that the initial reaction of Cp_2ZrCl_2 with *n*-BuLi generates "Cp_2Zr" in situ.[17] Oxidative addition of P–H gives the reactive species $Cp_2ZrH(PRH)$. Such intermediates have been observed in related reactions of "$Cp^*{}_2Zr$" with $CyPH_2$.[16] Hafnium analogues of these species have been isolated and structurally characterized by Vaughan and Hillhouse.[11] In the case of $Cp_2Zr(PPhH)H$, this Lewis acidic intermediate undergoes C–H activation, evolving H_2 and yielding a species in which η^5:η^1-cyclopentadienyl groups link two metal centers (**3**; Scheme I). Subsequent rearrangement with the formation of a C–C bond affords the product **1**. The proposal of the intermediate **3** is supported to some extent by the isolation of **2**, inasmuch as this species provides the first structural precedent for such η^5:η^1-cyclopentadienyl groups between Zr centers.[24] Further, Choukroun et al. have recently reported the preparation of the related species $[(CpZrCl)(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4)]_2$ via the thermolysis of Cp_2ZrHCl to $(CpZrCl)_2(\mu\text{-}\eta^5:\eta^5\text{-}C_{10}H_8)$,[25] while Gambarotta et al.[26] have described the synthesis of $(CpZrX)_2(\mu\text{-}\eta^5:\eta^5\text{-}C_{10}H_8)$ (X = SPh, Cl, Br) from a Zr(III) species formulated as $[CpZr(PMe_3)(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)]_2$.[27] The activation of C–H bonds by Zr(IV) centers is also supported in principle by recent reports of agostic H interactions with $Cp_2Zr(IV)$ centers.[28] In the case of **2**, the details of the mechanism of formation are not understood; however, it appears the steric demands of the substituent on $(2,4,6\text{-}t\text{-}Bu_3C_6H_2)PH_2$ preclude dimerization. Apparently, trimerization leads to a stabilization of the η^1:η^5-C_5H_4 links between the metal centers. The requisite cleavage of the P–C bond may be facilitated by the electron-deficient Zr centers. In a related sense, Carty et al.[29] have shown that the formally unsaturated ruthenium species $Ru_3(CO)_9(\mu\text{-}PPh_2)(\mu\text{-}H)$ exhibits a weak interaction between an electron-deficient Ru atom and one of the P–C bonds, which upon heating affords $Ru_5(CO)_{16}(\mu\text{-}PPh_2)(\mu\text{-}P)$ among other products. The details of this P–C bond activation and the mechanism of formation of **2** are currently under study. Further, the synthetic utility and the factors controlling P–H, C–H, and P–C bond activation in early-metal phosphides are being explored.

Acknowledgment. Financial support from the NSERC of Canada is gratefully acknowledged.

Registry No. **1**, 138858-82-9; **2**, 138858-84-1; Cp_2ZrCl_2, 1291-32-3; $PhPH_2$, 638-21-1; $(2,4,6\text{-}t\text{-}Bu_3C_6H_2)PH_2$, 83115-12-2.

Supplementary Material Available: Tables of crystallographic data, positional and thermal parameters for non-hydrogen atoms, hydrogen atom positional parameters, and bond distances and angles for **1** and **2** (10 pages); listings of $10F_o$ and $10F_c$ (23 pages). Ordering information is given on any current masthead page.

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(24) η^1:η^5-cyclopentadienyl groups are also present in $[Cp_2Th(\eta^5:\eta^1\text{-}Cp)]_2$,[30] $[CpNbH(\eta^5:\eta^1\text{-}Cp)]_2$,[31] and $[CpTi(PMe_3)(\eta^5:\eta^1\text{-}Cp)]_2$.[25]

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